

## TITLE OF THE INVENTION

### METHOD OF MAKING OXIDE FILM BY ANODIZING MAGNESIUM MATERIAL

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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention:

The present invention relates to a method of making a corrosion-resistant oxide film on a selected object, or target component, made of magnesium (as pure metal) or a magnesium alloy. The target component may typically be the housing of a notebook computer. The present invention also relates to a housing produced through such a method.

### 2. Description of the Related Art:

Recently, housings made of magnesium or a magnesium alloy have been widely used for providing electric or electronic appliances such as notebook computers, in order to achieve reduction in weight and thickness. This trend is particularly conspicuous in the field of the so-called mobile notebook computers whose size is equal to or smaller than the B5-size. Fig. 5 of the accompanying drawings shows an example of a housing of a portable device that is made of a magnesium material (i.e. magnesium as a pure metal or a magnesium alloy). Specifically, the illustrated component is an LCD(liquid crystal display) cover used for the housing of a notebook computer. As known in the art, a magnesium material is an excellent heat conductor. Thus, when used to make a housing of a notebook computer, the magnesium material contributes not only to achieving the weight and thickness reduction, but to preventing the electronic device

from overheating.

A magnesium material is readily oxidized when exposed to the air. Thus, for practical use, a magnesium-made housing needs to be subjected to a surface treatment to  
5 become corrosive resistant beforehand.

One of the known methods for providing corrosion resistance is chemical conversion. In a chemical conversion treatment, a magnesium material is immersed in a chemical bath to form a coating on the material. This method,  
10 however, relies on the spontaneous chemical reaction which will occur on the surface of the magnesium material. Therefore, the freedom of controlling the film thickness is significantly restricted. Another drawback of the known method is that the produced film tends to be small in  
15 thickness. Accordingly, it is difficult to improve the corrosion resistance on the surface of the magnesium material to a desired degree.

Anodizing is another known method, which can produce a thicker coating film than the above-described chemical  
20 conversion. A thicker and denser film is preferable for enhancing corrosion resistance. However, since the oxidation layer formed by the anodizing does not allow the passage of electricity, the fabrication of a thick film entails high voltage application and long production time.  
25 Unfavorably, this raises the production cost.

JP-A-8(1996)-167543 and JP-A-11(1999)-100695 disclose methods whereby a thick coating film can be made in a shorter time. Specifically, the former JP document teaches

that dielectric particles are included in an electrolyte used for performing an anodic oxidation treatment with respect to an aluminum surface. The latter JP document, on the other hand, teaches that metal particles are included in  
5 an electrolyte used for performing an anodic oxidation treatment with respect to a titanium surface.

It should be noted here that the above JP documents merely propose a method of making an anodic oxidation layer on the surface of aluminum or titanium material, but not on  
10 the surface of magnesium material. Further, the JP documents do not include any suggestion that their methods, which are characterized by the inclusion of dielectric or metal particles into an electrolyte, can be equally applied to a magnesium material.

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#### SUMMARY OF THE INVENTION

The present invention has been proposed under the circumstances described above. It is, therefore, an object of the present invention to provide a method of making a  
20 highly-anticorrosive anodic oxide film or layer on a magnesium material, whereby the desired oxide film can be formed in a short time and at low production costs.

According to a first aspect of the present invention, there is provided a method of making an oxide film. The  
25 method comprises: immersing an object into an electrolyte, the object being made of magnesium or a magnesium alloy; and forming an oxide film on the object in the electrolyte by anodizing. The electrolyte comprises insoluble particles

and alkali metal hydroxide. The oxide film takes in the insoluble particles as the film is growing on the object.

In accordance with the above method, an appropriately thick oxide film can be formed on the desired object in a shorter time than is conventionally possible, since the oxide film growing on the object takes in the insoluble particles contained in the electrolyte. With the oxidation film produced, the object of the magnesium material enjoys greater corrosion-resistance. Also, the production cost can be reduced due to the shortened film-forming time. Further, the electrolyte containing alkali metal hydroxide contributes to the acceleration of the oxide film to be produced (this advantageous effect is demonstrated in the examples to be described later). Still further, the alkali metal hydroxide is effective for preventing the segregation (localized precipitation) of the insoluble particles taken into the oxide film. As a result, a uniformly dense oxide film can be formed on the magnesium object.

Preferably, the insoluble particles may be made of at least one of alumina, aluminum hydroxide, silica, titanium oxide, and ceramic oxide. The average diameter of the particles may be in a range of 5nm~10 $\mu$ m, and more preferably in a range of 5nm~500nm.

The "insoluble particles" in this specification refer to particles which are not dissolved in the electrolyte. When the average diameter of the particles is greater than 10 $\mu$ m, proper (or even improper) precipitation of the particles on the magnesium object is less likely to occur.

In such an instance, the particle precipitation, if any, may make the surface of the oxide film unduly rough. Accordingly, at some places, the surface of the magnesium object may fail to be appropriately protected by the oxide  
5 film, thereby becoming susceptible to corrosion. According to preferred embodiments, the insoluble particles are made small enough to ensure proper precipitation on the magnesium object and to reduce the surface roughness of the oxide film.

Preferably, the anodizing may be performed by  
10 application of an alternating current having a current density in a range of  $2A/dm^2 \sim 5A/dm^2$ . When the current density is smaller than  $2A/dm^2$ , the insoluble particles may fail to be precipitated at all, or may segregate, if any. Also, spark discharge is less likely to occur with a small  
15 current density. Consequently, the resultant oxide film tends to be unduly small in thickness and density, which is disadvantageous for producing a highly corrosion-resistant oxide film in a short period of time. On the other hand, when the current density is greater than  $5A/dm^2$ , the  
20 resultant oxide film tends to have an unduly rough surface. Accordingly, the corrosion resistance of the film is reduced, whereas the production cost of the film is increased due to the high current density.

Preferably, the frequency of the alternating current to  
25 perform the anodizing may be in a range of  $40Hz \sim 80Hz$ . When the frequency is lower than  $40Hz$ , the insoluble particles in the electrolyte tend to segregate on the magnesium object. On the other hand, when the frequency is higher than  $80Hz$ ,

the forming rate of the oxide film is liable to reduce significantly.

Preferably, the electrolyte for performing the anodizing may be kept at a temperature in a range of 5 15°C~60°C. Temperatures lower than 15°C decrease the film forming rate significantly, while temperatures higher than 60°C make the surface of the oxide film unduly rough.

Preferably, the alkali metal hydroxide in the electrolyte may have a concentration in a range of 10 25g/dm<sup>3</sup>~75g/dm<sup>3</sup>. When the concentration is smaller than 25g/dm<sup>3</sup>, the insoluble particles tend to segregate in precipitation, and the film forming rate reduces. When the concentration is greater than 75g/dm<sup>3</sup>, no further improvement cannot be expected than when the concentration 15 lies in the range of 25g/dm<sup>3</sup>~75g/dm<sup>3</sup>.

Preferably, the electrolyte may comprise an aqueous solution of a soluble silicate or oxyacid salt. The aqueous solution of such a substance is a suitable electrolyte for causing spark discharge necessary for performing the 20 anodizing.

Preferably, the soluble silicate in the electrolyte may have a concentration in a range of 100g/dm<sup>3</sup>~250g/dm<sup>3</sup>, while the oxyacid salt in the electrolyte may have a concentration in a range of 75g/dm<sup>3</sup>~150g/dm<sup>3</sup>. When these concentrations 25 are smaller than the respective minimum values (i.e. 100g/dm<sup>3</sup> and 75g/dm<sup>3</sup>), no spark discharge occurs at all, or an unduly long time may need to pass before any spark discharge starts to occur. On the other hand,

concentrations greater than the maximum values (i.e. 250g/dm<sup>3</sup> and 150g/dm<sup>3</sup>) may not be practical since no additional advantage is obtained due to the excessive amounts of silicate or oxyacid salt.

5        Preferably, the method of the present invention may further comprise a step of forming a coating layer on the oxide film, the coating layer being made of at least one of an organic material, an inorganic material, and a metal oxide sol. The coating layer serves for protective and  
10 decorative purposes. Also, the coating layer serves to close up pores in the oxidation film.

According to a second aspect of the present invention, there is provided a housing that comprises: a housing body made of a magnesium material; and an oxide film formed on  
15 the body. The oxide film may contain particles made of at least one of alumina, aluminum hydroxide, silica, titanium oxide, and ceramic oxide. These particles are taken into the oxide film when the film is caused to grow on the body by anodizing.

20        Other features and advantages of the present invention will become apparent from the detailed description given below with reference to the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

25        Fig. 1 is a flow chart showing the procedure of an oxide film fabrication method according to the present invention;

Fig. 2 schematically shows an oxidation processing apparatus used for implementing the method of the present invention;

Fig. 3 is a graph showing the surface roughness and thickness of oxidation films produced under different conditions of electrolysis;

Fig. 4 is a graph showing the thickness of oxidation films produced with the use of different electrolytes; and

Fig. 5 shows a housing made of a magnesium material for a portable electronic device.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will be described below with reference to the accompanying drawings.

Fig. 1 shows a flow chart illustrating an anodic oxide film fabrication method according to a preferred embodiment of the present invention. As will become clear from the following explanation, the method of the present invention makes it possible to form a highly-anticorrosive anodic oxide film on an object made of a magnesium material. In this specification, the "magnesium material" refers to magnesium as a pure metal or to a magnesium alloy. As shown in the flow chart, the method includes a degreasing step S11, a first rinsing step S12, an anodic oxidizing step S13, a second rinsing step S14, a nitrogen blowing step S15, a coating step S16, and a baking step S17.

Examples of magnesium alloys are Mg-Al alloy, Mg-Al-Zn alloy, Mg-Al-Mn alloy, Mg-Zn-Zr alloy, Mg-(rare earth



element) alloy, Mg-Zn-(rare earth element) alloy, and so on. More specifically, they are AZ91D alloy, AZ31 alloy, AZ61 alloy, AM60 alloy, and AM120 alloy, for example. With these magnesium materials, an object or component as shown in Fig.

5 5 can be produced. The obtained object is then coated with an anodic oxide film.

Referring to the flow chart of Fig. 1, the anodic oxide film fabrication method may proceed in the following manner.

In the first step S11, an object of a magnesium  
10 material is subjected to a degreasing treatment, in which the object is dipped into an acetone bath and then put into an alkaline processing solution. For the alkaline processing solution, use may be made of sodium carbonate, sodium hydroxide, or potassium hydroxide, for example. It  
15 is possible to perform the degreasing by applying a surface-active agent to the object to be treated. An example of the surface-active agent is sodium dodecylbenzenesulfonate.

In the second step S12, the degreased object is rinsed with running water for removing a remnant of the agents used  
20 for the degreasing treatment. According to the present invention, the first and second steps S11, S12 (collectively referred to as a "preliminary process") may be followed by an etching step and an acid cleaning step. The preliminary process is optional, and does not need to be performed, for  
25 example, when the object to be treated is sufficiently clean.

In the third step S13, the surface of the object to be treated is subjected to anodic oxidation. This process utilizes an appropriate electrolyte, i.e. an aqueous

solution of one or more kinds of reagents for forming the desired oxide film. According to the present invention, the electrolyte preferably contains insoluble particles and alkali metal hydroxides. Examples of the film-forming reagents are soluble silicates (such as sodium silicate or sodium metasilicate) or oxyacid salts (such as trisodium phosphate or sodium aluminate). The concentration of the soluble silicates in the electrolyte may lie in a range of 100~250g/dm<sup>3</sup>. The concentration of the oxyacid salts in the electrolyte may be in a range of 75~150g/dm<sup>3</sup>. The particles, which are insoluble in the electrolyte, may be made of alumina, aluminum hydroxide, silica, titanium oxide, or ceramic oxide, for example. The average diameter of the insoluble particles may be in a range of 5nm~10µm, preferably no greater than 500nm. Examples of the alkali metal hydroxides are sodium hydroxide and potassium hydroxide. The concentration of the alkali metal hydroxide in the electrolyte may lie in a range of 25~75g/dm<sup>3</sup>.

Reference is now made to Fig. 2 illustrating anodic oxidation processing apparatus. As shown, the apparatus includes a power source 1 provided with two (or more) power supply terminals. One of the power supply terminals is connected to an electrode 2, while the other power supply terminal is connected to an electrode 3 which may be made of stainless steel or carbon. The paired electrodes 2 and 3 are dipped into an electrolyte 4 (which has been prepared to meet the requirements noted above). In this state, alternating voltage is applied between the electrodes 2 and

3, with the current density lying in a range of  $2\sim 5\text{A/dm}^2$ . A current density smaller than  $2\text{A/dm}^2$  tends to prevent proper spark discharge from occurring. In addition, with such a small current density, the insoluble particles may fail to precipitate at all on the object electrode 2, or may precipitate unevenly, or segregate, on the electrode 2. When the current density is greater than  $5\text{A/dm}^2$ , on the other hand, the surface of the produced oxide film may become unacceptably rough. The temperature of the electrolyte 4 is adjusted to lie in a range of  $15\sim 60^\circ\text{C}$ , for example. When the temperature is lower than  $15^\circ\text{C}$ , the forming rate of the oxide film may be unduly low. When the temperature is greater than  $60^\circ\text{C}$ , the surface of the produced oxide film may become unacceptably rough. The frequency of the applied voltage may lie in a range of  $40\sim 80\text{Hz}$ , for example. When the frequency is smaller than  $40\text{Hz}$ , the insoluble particles tend to segregate on the object electrode 2. When the frequency is greater than  $80\text{Hz}$ , the forming rate of the oxide film may become significantly slow. For uniformly dispersing the insoluble particles in the electrolyte, the illustrated anodic oxidation processing apparatus includes a magnetic stirrer 5 and a rotator 6. In operation, as shown in the figure, the rotator 6 is put in the electrolyte 4, and can be driven to rotate by the stirrer 5 through the magnetic force.

By the anodic oxidation processing, spark discharge occurs on the surface of the object to be treated, whereby the desired oxide film gradually grows. During its growth,

the oxide film takes in the insoluble particles from the electrolyte. Due to this, the forming rate of the film is faster than when no such insoluble particles are included. Further, in the presence of the alkali metal hydroxide in the electrolyte, the forming rate of the film can be much greater, and the uneven precipitation of the insoluble particles can be prevented. In the preferred embodiment of the present invention, it is possible to form an anodic oxide film to a thickness of 20~40  $\mu\text{m}$  in 10~30 minutes.

10 In the fourth step S14, the anodized object electrode is rinsed with running water to remove the remaining electrolyte on the electrode.

In the fifth step S15, nitrogen gas is blasted against the object electrode for blowing off or vaporizing the water on the electrode.

In the sixth step S16, a fluid coating agent is applied over the anodic oxide film on the object electrode by spin-coating, dip-coating, doctor-blading, or roll-coating, for example. The coating agent may be a commercially available, organic or inorganic substance, or a metal oxide sol that can be hardened by a solgel method.

20 In the seventh step S17, the applied coating agent is hardened. To this end, the object electrode with the coating agent applied is kept at room temperature for about ten minutes, and then heated in an oven at about 120°C for 30~60 minutes. The thus obtained coating layer protects the anodic oxide film from physical damage, while also making the object electrode glossy. When no such coating layer is

required, the steps S16 and S17 are not performed.

According to the anodic oxide film fabrication method of the present invention, as noted above, the oxide film on the magnesium material can take in nearby insoluble particles dispersed in the electrolyte. Therefore, the desired thickness of the oxide film can be attained in a shorter period of time than when use is made of an electrolyte containing no such insoluble particles. Advantageously, the time taken for attaining the desired film thickness can still be shortened by the addition of alkali metal hydroxide into the electrolyte. Further, the added alkali metal hydroxide promotes uniform precipitation of the insoluble particles, thereby preventing the segregation of the particles precipitated. According to the present invention, it is possible to produce a uniformly dense oxide film on the target object.

Several examples and a comparative sample will now be described below.

#### Example 1

##### 20 <Electrolyte Preparation>

An electrolyte was prepared, which contained 100g/dm<sup>3</sup>(grams per liter) sodium aluminate (available from Kanto Kagaku), 25g/dm<sup>3</sup> sodium hydroxide (available from Wako Pure Chemical Industries), and 10% aluminum hydroxide (available from Wako Pure Chemical Industries).

##### <Oxidation Film Forming Procedure>

A plate of a magnesium alloy AZ31 (available from Toyo Mark; Size 70mm×20mm×1.5mm) was subjected to degreasing (S11

in Fig. 1) and first rinsing (S12). Then, as in the manner shown in Fig. 2, the plate was immersed in the prepared electrolyte, together with an associated plate made of stainless steel SUS-304. An alternating voltage (current density:  $4\text{A/dm}^2$ ) was applied to the AZ31 plate and the SUS-304 plate for ten minutes. At this time, the magnetic stirrer was operated to stir the electrolyte at a rate of 400rpm(revolutions per minute), with the temperature of the electrolyte kept at  $30^\circ\text{C}$ . Thereafter, the AZ31 plate was taken out from the electrolyte, and rinsed with running water (second rinsing S14). Then, the AZ31 plate was dried by nitrogen blowing (S15). As a result, the AZ31 plate was coated with an oxide film containing aluminum hydroxide. The thickness of the produced film was  $30\mu\text{m}$ .

## 15      Example 2

### <Electrolyte Preparation>

An electrolyte was prepared, which contained  $200\text{g/dm}^3$  sodium metasilicate (available from *Wako Pure Chemical Industries*),  $50\text{g/dm}^3$  sodium hydroxide (available from *Wako Pure Chemical Industries*); and 10% aluminum oxide (available from *Furuuchi Chemical*).

### <Oxidation Film Forming Procedure>

A plate of a magnesium alloy AZ31 (available from *Toyo Mark*; Size  $70\text{mm}\times 20\text{mm}\times 1.5\text{mm}$ ) was subjected to degreasing (S11 in Fig. 1) and first rinsing (S12). Then, as in the manner shown in Fig. 2, the plate was immersed in the prepared electrolyte, together with an associated plate made of stainless steel SUS-304. An alternating voltage (current

density:  $4\text{A/dm}^2$ ) was applied to the AZ31 plate and the SUS-304 plate for ten minutes. At this time, the magnetic stirrer was operated to stir the electrolyte at a rate of 400rpm, with the temperature of the electrolyte kept at  $30^\circ\text{C}$ .  
5 Thereafter, the AZ31 plate was taken out from the electrolyte, and rinsed with running water (second rinsing S14). Then, the AZ31 plate was dried by nitrogen blowing (S15). Further, the AZ31 plate was dipped into an inorganic coating agent, or heatless glass (available from Ohashi  
10 Chemical Industries; Trade name GS-600-1 type BC), and taken out from the coating agent at a rate of  $3\text{m/s}$ . Then, after kept at room temperature for 30 minutes, the AZ31 plate was dried in an oven at  $120^\circ\text{C}$  for 60 minutes. Thus, a coating layer was formed over the oxide film on the AZ31 plate. The  
15 oxide film was  $30\mu\text{m}$  in thickness and contained aluminum oxide.

#### Examples 3~6 and Comparative sample

##### <Electrolyte Preparation>

For Examples 3~6, an electrolyte was prepared, which  
20 contained  $200\text{g/dm}^3$  sodium metasilicate (available from Wako Pure Chemical Industries),  $50\text{g/dm}^3$  sodium hydroxide (available from Wako Pure Chemical Industries), and 5% aluminum oxide (available from Furuuchi Chemical). For Comparative sample, on the other hand, an electrolyte was  
25 prepared, which contained  $200\text{g/dm}^3$  sodium metasilicate (available from Wako Pure Chemical Industries).

### <Oxidation Film Forming Procedure>

For each of the examples and the comparative sample, a plate of a magnesium alloy AZ31 (available from *Toyo Mark*; Size 70mm×20mm×1.5mm) was subjected to degreasing (S11 in Fig. 1) and first rinsing (S12). Then, as in the manner shown in Fig. 2, the plate was immersed in the electrolyte prepared for Examples 3~6 or Comparative sample, together with an associated plate made of stainless steel SUS-304. The temperature of the electrolyte was kept at 30°C. The electrolyte was stirred by the magnetic stirrer at a rate of 400rpm. Depending on the examples or the comparative sample, the following current density and processing time (i.e. voltage application time) were employed for oxide film forming. Specifically, for Example 3, the current density was 2A/dm<sup>2</sup> and the processing time was 15 minutes. For Example 4, the current density was 2A/dm<sup>2</sup> and the processing time was 30 minutes. For Example 5, the current density was 4A/dm<sup>2</sup> and the processing time was 7.5 minutes. For Example 6, the current density was 8A/dm<sup>2</sup> and the processing time was 3.8 minutes. For Comparative sample, the current density was 2A/dm<sup>2</sup> and the processing time was 15 minutes. After the voltage application was performed for the prescribed time, the AZ31 plate was taken out from the electrolyte, and then rinsed with running water (S14). The rinsed plate was dried by nitrogen blowing (S15).

### <Evaluation of Produced Oxidation Film>

Fig. 3 is a graph showing the relative thickness and relative surface roughness of the oxide films produced by



Examples 3~6. Specifically, in the graph, the respective oxide film thicknesses of Sample and Examples 3~6 (see the black dots) are represented as relative values to the film thickness of Sample. (Hence, the relative film thickness of Sample is 1). On the other hand, the surface roughness of each case is represented by a shaded bar. The surface roughness is also a relative value obtained by the comparison with a bare reference plate made of the magnesium material. In the graph, the reference plate has a unit surface roughness (i.e. 1) depicted by the rightmost bar.

As seen from the graph, the oxide film thickness of Example 3 (with the use of an electrolyte containing alumina particles and sodium hydroxide) is about five times larger than that of Comparative sample (with the use of an electrolyte containing no alumina particles nor sodium hydroxide). As noted above, the voltage application times for Example 3 and Comparative sample are both 15 minutes. This means that the oxide film forming rate of Example 3 is about five times faster than that of Comparative sample. Further, the graph shows that a greater current density is responsible for a faster film forming rate (see Examples 3, 5 and 6) and for a greater surface roughness of the obtained oxide film. In particular, the surface roughness of Example 6 is more than five times greater than that of the non-coated reference plate, which is not acceptable. As seen from Examples 3 and 4, a longer film forming time (voltage application time) increases the surface roughness of the oxide film.

### Examples 7 and 8

#### <Electrolyte Preparation>

For Example 7, an electrolyte was prepared, which contained 200g/dm<sup>3</sup> sodium metasilicate (available from *Wako Pure Chemical Industries*) and 5% aluminum oxide (available from *Furuuchi Chemical*). For Example 8, an electrolyte was prepared, which contained 200g/dm<sup>3</sup> sodium metasilicate (available from *Wako Pure Chemical Industries*), 50g/dm<sup>3</sup> sodium hydroxide (available from *Wako Pure Chemical Industries*), and 5% aluminum oxide (available from *Furuuchi Chemical*).

#### <Oxidation Film Forming Procedure>

For each of Examples 7 and 8, a plate of a magnesium alloy AZ31 (available from *Toyo Mark*; Size 70mm×20mm×1.5mm) was subjected to degreasing (S11 in Fig. 1) and first rinsing (S12). Then, as in the manner shown in Fig. 2, the plate was immersed in the prepared electrolyte, together with an associated plate made of stainless steel SUS-304. An alternating voltage (current density: 2A/dm<sup>2</sup>) was applied to the AZ31 plate and the SUS-304 plate for 15 minutes. At this time, the magnetic stirrer was operated to stir the electrolyte at a rate of 400rpm, with the temperature of the electrolyte kept at 30°C. Thereafter, the AZ31 plate was taken out from the electrolyte, and rinsed with running water (second rinsing S14). Then, the AZ31 plate was dried by nitrogen blowing (S15).

<Evaluation of Produced Oxidation Film>

Fig. 4 is a graph showing the oxide film thicknesses for Example 7 and Example 8, represented in comparison with the thickness of Example 7 (hence the relative thickness of Example 7 is 1). As seen from the graph, the addition of sodium hydroxide to the electrolyte (Example 8) makes the film thickness 3.67 times greater in the same voltage application time than when no such addition is performed (Example 7).

The present invention being thus described, it is obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the present invention, and all such modifications as would be obvious to those skilled in the art are intended to be included within the scope of the following claims.